consequence of the relatively high ionization constant of the carboxyl groups; the base side behaves normally as shown in the inset of Fig. 2.

A series of further papers on the potentiometric behavior of this polymer, ion-binding by the polymer and other studies is in preparation.

The authors wish to thank Professor K. G. Stern who performed the electrophoresis experiments.

This investigation was supported in part by the Office of Naval Research and by a research grant, RG 2934(C3) from the Division of Research Grants of the National Institutes of Health, Public Health Service.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

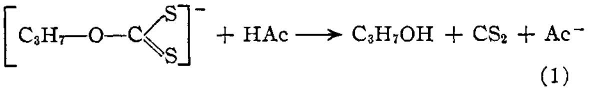
Kinetics of the Decomposition of *n*-Propylxanthic Acid[1]

BY MELVIN L. SCHOCHET AND CECIL V. KING

RECEIVED APRIL 12, 1955

The rate of decomposition of *n*-propylxanthic acid has been determined at five temperatures from 0 to 60°, in dilute acetic acid–sodium acetate buffers containing up to 30% 1,4-dioxane to vary the dielectric constant. Electrostatic effects on the observed rates are small, because primary effects (on the kinetics of the rate-controlling process) and secondary effects (on the buffer equilibrium) are about equal and opposite in sign. Activation energies and entropies are discussed.

The decomposition reaction of *n*-propyl xanthate in acetic acid buffers may be written



$$\left[C_3H_7{-}O{-}C\begin{matrix}\diagup S\\ \diagdown\!\!\diagdown S\end{matrix}\right]^- + HAc \longrightarrow C_3H_7OH + CS_2 + Ac^- \qquad (1)$$

While the xanthic acids are not quite fully ionized,[2] essentially only the ions are present in these buffers. Equation 1 does not represent the mechanism, since the rate depends on the buffer ratio, not on the acid component alone.[3] There is no general acid or base catalysis which can be detected in dilute aqueous solution. In previous studies of ethylxanthic acid[3,4] both salt and dielectric constant effects were found to be small, if the low dielectric constant region of ion pair formation is avoided.

The present work was undertaken partly in order to compare another xanthic acid with methyl-[2] and ethylxanthic[2–4] acids, with respect to absolute decomposition rates and general behavior, partly to extend the temperature range of such measurements. No appreciable change in activation energy was found over the 60° range explored.

Experimental

Potassium *n*-propyl xanthate was prepared by mixing a solution of potassium hydroxide in the alcohol with carbon disulfide in ethyl ether. The salt was washed with ether and recrystallized from acetone with addition of ether. Its purity was confirmed by titrating weighed samples with standard iodine solution.

Acetic acid buffers, and pure dioxane, were prepared as described before.[4] Two solutions were made up and allowed to come to temperature in the thermostat: (a) the buffer, double strength, and (b) the xanthate in water or water-dioxane. Then 250-ml. portions of both were poured simultaneously into a larger flask mounted in the thermostat. In each run, seven to ten samples were withdrawn over a two- to five-hour period, quenched with sodium bicarbonate, and the remaining xanthate titrated with standard iodine solution.[2] The reaction was usually 75% complete in the time allowed.

Rate constants were calculated by means of the equation[3]

$$kK_0 = \frac{2.3}{(b-a)t}\left[(a+c)\log\frac{a}{a-x} - (b+c)\log\frac{b}{b-x}\right] \qquad (2)$$

where a, b, c, are initial concentrations of xanthate, acetic acid and acetate, respectively, and K_0 is the thermodynamic dissociation constant of acetic acid.

Two to five runs were made at each concentration and temperature. The initial xanthate concentration was usually 0.012 to 0.015 *M*. The sodium acetate was made 0.01 to 0.04 *M*, and acetic acid–acetate ratios of 0.5 to 8 served to keep the rate in a convenient range. Rate constants showed no trend with extent of reaction; the average deviation in single runs and of several runs was usually less than 3.5%. Runs with added sodium chloride showed the salt effect to be small, as expected.

The dioxane mixtures were made by volume at room temperature, the weight concentrations and mole fractions calculated from the densities. The temperatures were maintained to ±0.02°, 0° referring to an ice-bath temperature of about +0.015°.

Experimental Results

The rate constants obtained, without regard to K_0 for acetic acid, are summarized in logarithmic form in Table I.

TABLE I

LOG OF RATE CONSTANTS, kK_0, MIN.$^{-1}$

Wt. % dioxane →	0	10.2	20.2	30.1	Eq. 3
0°	−3.44	−3.47	−3.40	−3.50	−3.47
15°	−2.81	−2.78	−2.75	−2.76	−2.76
30°	−2.14	−2.14	−2.12	−2.10	−2.12
45°	−1.57	−1.48	−1.43	−1.44	−1.52
60°	−0.99	−1.11	−1.05	−0.99	−1.00

Equation 3 is the least squares relation for the averages at each temperature *vs.* $1/T$

$$\log kK_0 = 10.24 - 17140/2.3RT \qquad (3)$$

This equation represents all the data with an average deviation of 0.033 log unit. The maximum deviation of 0.11 log unit represents 22% in the value of kK_0.

The rate constants found are remarkably similar to those for the decomposition of ethyl xanthic acid in similar buffers,[4] for example at 30° the average value for the ethyl compound was $\log kK_0 = -2.19$.

Discussion

While equation 3 represents the rate constants kK_0 within the apparent over-all experimental error in this range, it is unsatisfactory from a theoretical view-point. Since values of K_0 are available, the bimolecular constants k may be calculated.

---

[1] From a Ph.D. thesis submitted by Melvin L. Schochet to the Graduate Faculty of New York University in April, 1954.

[2] H. v. Halban and W. Hecht, *Z. Elektrochem.*, **24**, 65 (1918).

[3] C. V. King and E. Dublon, THIS JOURNAL, **54**, 2177 (1932).

[4] A. Chatenever and C. V. King, *ibid.*, **71**, 3587 (1949).

These correspond to the mechanism assumed in deriving equation 2

$$ROCS_2^- + H^+ \longrightarrow X^0 \longrightarrow \text{products} \qquad (4)$$

According to the Christiansen–Scatchard equation, written without the Brønsted salt effect term

$$\log k = \log k_\infty - \frac{Z_A Z_B \epsilon^2}{2.3kTDr} \qquad (5)$$

log k should be a linear function of $1/D$ at each temperature.[5] If kK_0 were truly independent of the dielectric constant D, log K_0 should be linear with $1/D$ with slope of opposite sign; this is not true even over the range considered here.

Since K_0 and D are known much more precisely than kK_0 from the rate measurements, equation 3 must be taken as an approximation, and in calculating activation energies for process (4), or rate constants freed from electrostatic effects, the experimental data should be used rather than equation 3.

We have calculated log k, obtaining log K_0 from the equations of Harned and Fallon.[6] Extrapolation to 60° is required and the following equation was used

$$\log K_0 = -4.82 - 11.59N \text{ at } 60° \qquad (6)$$

where N is the mole fraction dioxane. The dielectric constant D is easily interpolated from the data of Åkerlöf and Short.[7] From plots of log k *vs.* $1/D$, equation 5, which are linear within experimental error, the critical complex radius r was determined to be 1.72 ± 0.07 Å., a value near that found for ethyl xanthate.[4]

Table II gives activation energies E_{expt} and the Arrhenius log A from the least squares equations for log k *vs.* $1/T$. Since $E_{expt} = \Delta H^* + RT = \Delta E^* + RT$, the "absolute rate" equation becomes

$$k = 60e\frac{kT}{h}\exp\left(-\frac{E_{expt}}{RT}\right)\exp\left(-\frac{\Delta S^*}{R}\right) \qquad (7)$$

(where 60 enters because k is in liter mole^{-1} min.$^{-1}$). The contribution of D to E_{expt} and ΔS^* can be calculated from equations given in the references cited,[5] and consequently E_∞ and ΔS^*_∞ values freed from electrostatic effects can be calculated. These are included in Table II.

TABLE II

ENERGY AND ENTROPY OF ACTIVATION

Dioxane, wt. %	log A	$E_{expt.}$, cal./mole	E_∞, cal./mole	ΔS^*, 303°K.	ΔS^*_∞, 303°K.
0	15.09	17250	16200	0.37	−11.37
10.2	15.20	17100	15750	0.87	−12.91
20.2	15.57	17100	14850	2.56	−13.97
30.1	16.67	18150	15800	7.58	−12.78

The values of E_∞ and ΔS^*_∞ should be constant independently of the solution from which the calculation is made. While E_∞ is no more constant than E_{expt}, ΔS^*_∞ is satisfactory. The values are somewhat larger numerically than was found for ethyl xanthate.

Comparison with collision theory may be made through the equation

$$\log PZ_0 = \log 60e\frac{kT}{h} + \frac{\Delta S^*_\infty}{2.3R} \qquad (8)$$

At 303°K., the right side = 15.01 − 2.79 = 12.22. Now

$$Z_0 = \frac{60N}{1000}\sigma^2\left[\frac{8\pi RT}{\mu}\right]^{1/2} \qquad (9)$$

Using $\sigma = 1.72$ Å. and $\mu = (135 \times 19)/154 = 16.66$

$$\log Z_0 = 12.37$$

As is usual for this type of reaction, there is no great discrepancy.

NEW YORK, N. Y.

---

(5) This and other equations used may be found in (a) E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, 1949; (b) J. C. Warner, *Ann. N. Y. Acad. Sci.*, **39**, 345 (1940).

(6) H. S. Harned and L. D. Fallon, THIS JOURNAL, **61**, 2377 (1939).

(7) G. Åkerlöf and O. A. Short, *ibid.*, **58**, 1241 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE A. AND M. COLLEGE OF TEXAS]

Rates of Reaction of Diphenyldiazomethane with Aliphatic Carboxylic Acids in Toluene[1]

BY A. BERNARD HOEFELMEYER AND C. KINNEY HANCOCK

RECEIVED APRIL 26, 1955

Rate constants at 25° have been determined for the reaction of diphenyldiazomethane with 28 carboxylic acids in toluene. Statistical treatment of fifteen log k_2 values for which Taft's σ^*-values are available yields the following results: (1) equation of the regression line, log $k_2 = -0.603 + 2.80\ \sigma^*$, where 2.80 is the reaction constant ρ^*; (2) standard deviation from the regression line, 0.0941; (3) correlation coefficient, 0.998. Use of the equation, $\sigma^* = 0.215 + 0.356 \log k_2$, yields hitherto unreported σ^*-values for 11 substituents. The anomalous cases of formic and benzoic acids are discussed. The relatively large ρ^*-value of 2.80 may be of value in determining small differences in polarity.

Introduction

Taft[2] has proposed an equation, $\log k/k_0 = \sigma^*\rho^*$, for correlating polar substituent constants with rate or equilibrium constants for aliphatic reaction series having essentially constant steric and resonance factors. This equation is quite similar to that of Hammett,[3] $\log k - \log k^0 = \rho\sigma$, which has been applied so widely to reactions of *m*- and *p*-substituted benzene derivatives.

The present study was undertaken in order to determine if the Taft equation is applicable to the rates of reaction of diphenyldiazomethane (DDM) in toluene at 25° with carboxylic acids. This research was carried out independently of, but more or less parallel to, that of Taft and Smith[4] who studied the reactions of DDM in ethanol at 25° with 13 carboxylic acids, seven of which were included in the present study.

---

(1) Abstracted from the Ph.D. dissertation of A. B. Hoefelmeyer, The A. and M. College of Texas, 1954. Celanese Corporation of America, Clarkwood, Texas.

(2) R. W. Taft, Jr., THIS JOURNAL, **75**, 4231 (1953).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

(4) R. W. Taft, Jr., and D. J. Smith, THIS JOURNAL, **76**, 305 (1954).